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XRF and powder X-ray diffraction analysis of ancient iron slags from the "Sladak Kladenets" and "Malko Dryanovo" archaeological sites, Bulgaria

XRF и рентгено-фазов анализ на древни железни шлаки от археологически обекти „Сладък кладенец“ и „Малко Дряново“, България

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Abstract. Using X-ray fluorescence and Powder X-ray diffraction analysis, the chemical and phase composition of ancient iron slags and raw iron ore were investigated. The type of raw ore was identified as self-fluxing. The operating furnace temperature was determined in the range 900–1000 °C. The results obtained are of archaeological importance. They will contribute to the chronological specification of the time of realization of the metallurgical process and the type of used furnaces.

Keywords: ancient iron slags, XRF, phase analysis.

Introduction

The melting point of pure iron is about 1550 °C, a temperature that was unattainable in ancient times due to the absence of high-calorie fuel and imperfect furnace designs. The iron was extracted in the solid-state by a reduction process at a maximum temperature of about 1200 °C (Larreina-Garcia et al., 2018). The process involved the reduction of a portion of the iron oxides to form a solid metallic spongy iron mechanically mixed with the slag. In reduction furnaces, iron oxides react with CO emanating from the carbon fuel (charcoal). The charcoal is also a reducing agent in the system (Portillo-Blanco et al., 2020). Flux (limestone, quartz sand, sandstone) is often added to furnaces to lower the temperature of the iron reduction process and increase the rate of iron extraction. The reduction of iron started from about 800 °C but never reached the temperature of iron melting (Portillo-Blanco et al., 2020). This method of iron production determines the mainly ferro-silicate composition of the slag, which is close to fayalite, formed by the reaction of FeO from the ore and Si from quartz (Friede et al., 1982; Portillo-Blanco et al., 2020). The slag phase composition was controlled by the raw ore composition, furnace lining, addition of flux, but also by the design of the furnace - the way of air supply. Air was supplied through several holes in the walls of the furnace. In other constructions of furnaces for air supply ceramic tubes were inserted. This reduction method of iron extraction is known as the direct method of iron production (Portillo-Blanco et al., 2020; Roberts et al., 2014).

The phase composition of ancient slags provides information on temperature and air control in an ancient reduction furnace. These data are significant for archaeological interpretations. Based on them, the chronological specification of the time of realization of the metallurgical process and the type of used furnace can be done (Roberts et al., 2014).

Ancient iron slags were found in many places in Bulgaria. The investigations on slag's phase composition are sporadic regardless of informativeness. This

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work deals with the study of chemical and phase composition investigations of ancient iron slags from the "Sladak Kladenets" and "Malko Dryanovo" archaeological sites (Bulgaria) and raw ore from the Sarnevets hematite deposit, located close to them. The aim is to establish some conditions of the iron production process of archaeological importance – namely, temperature and air control in an ancient reduction furnace. For this purpose, X-ray fluorescence and Powder X-ray diffraction analysis were used.

Materials and methods

Two iron slags were studied – one from the "Sladak Kladenets" site (sample No 116) and one from the "Malko Dryanovo" site (sample No 131). The archeological sites are situated close to the Sarnevets hematite ore deposit, where the ore bodies outcrop on the earth's surface. Traces of ancient ore mining are also described (Kanurkov, 1988; Tsankov et al., 1995). The hematite sample from that deposit (sample No 112) was investigated as raw ore for ancient iron production. The slag samples were found on the earth's surface, but the furnaces for iron production were not found. In chronological terms, it is assumed that the metallurgical process here was carried out with high probability during the Late Roman Age, Late Antiquity, and the Middle Ages. The possibility for iron production during the second half of the first millennium BC should not be ruled out (Uzunov et al., 2017).

X-ray fluorescence (XRF) analysis was performed in the Center for Archaeometry with Laboratory of restoration and conservation of Sofia University "St. Kl. Ohridski" by energy dispersive Micro-XRF Spectrometer M1 MISTRAL, Bruker (Rh-tube, Peltier cooling, 30 mm², Si-drift detector (SDD), MnKα resolution <150 eV, collimator 0.1 mm to 1.5 mm), additionally calibrated with external standards. The samples were prepared as pressed pellet with H_3BO_3 binder (1 g sample + 0.5 g H_3BO_3).

The powder X-ray diffraction (PXRD) measurements were made in the Institute of Mineralogy and Crystallography "Acad. I. Kostov" at Bulgarian Academy of Sciences by Empyrean, "Panalytical", CuKα radiation (λ = 0.15418 nm) (operating at 40 kV, 30 mA) from 5 to 90° 2θ with a step of 0.013 2θ, 30 s/step with the pulse height distribution (PHD) refinement, starting from 25, 30, 35, 40, 41 to 51% and the optimal value selection.

Results and discussion

The results from the XRF analysis are shown in Table 1. The measured Fe_2O_3 in the hematite ore (sample No 112) was 56.31 wt%, and the SiO_2 – 34.5 wt% which suggests the presence of silicate minerals in the ore. The measured Fe_2O_3 in the samples 116 and 131 were 44.90 wt% and 51.46 wt%, respectively. The quantity of TiO_2, SO_3, and MnO are very close at all samples. The concentration of MgO in the ore exceeds the MgO in slag samples. That suggests Mg incorporation into the final metallurgical product – spongy iron. The K_2O, Na_2O, and CaO in slags have similar values but are lower in the ore sample 112. K, Na, and Ca were incorporated in the slags from furnace fuel – charcoal (Kramar et al., 2015).

The results from PXRD analysis (Fig. 1) show the following phase composition of sample 112: hematite PDF#33-0664 (PDF, 2001), quartz PDF#08-7653 (PDF, 2001) and magnetite-PDF#75-1372 (PDF, 2001), which correspond with the results from XRF (Table 1). Both slag samples are composed of fayalite PDF#76-5937 (PDF, 2001), wustite PDF#46-1312 (PDF, 2001), leucite (Palmer et al., 1997), and quartz. The increased amount of K in the slag (Table 1) is sourced from the charcoal and leads to the leucite crystallization (Kramar et al., 2015). Only in sample 116, the maghemite PDF#39-1346 (PDF, 2001) was registered (Fig. 1).

The fayalite formation in slags shows enough quartz in the furnace to provide its crystallization (Portillo-Blanco et al., 2020). The close concentration of Si in all studied samples (Table 1) suggests no flux was added in the furnace, as the ore was self-fluxing.

The wustite crystallization in slags evidences a low degree of iron extraction from the ore (Manasse et al., 2002; Portillo et al., 2018) which corresponds to the XRF measurements (Table 1). The detected wustite and fayalite in slags suggest a furnace temperature of 560–1200 °C, and 1000–1100 °C, respectively (Portillo et al., 2018). It has been found that the presence of quartz allows the reduction of iron to take place at a temperature of about 1140 to 890 °C (Manasse et al., 2002; Portillo-Blanco et al., 2020). It can be as-

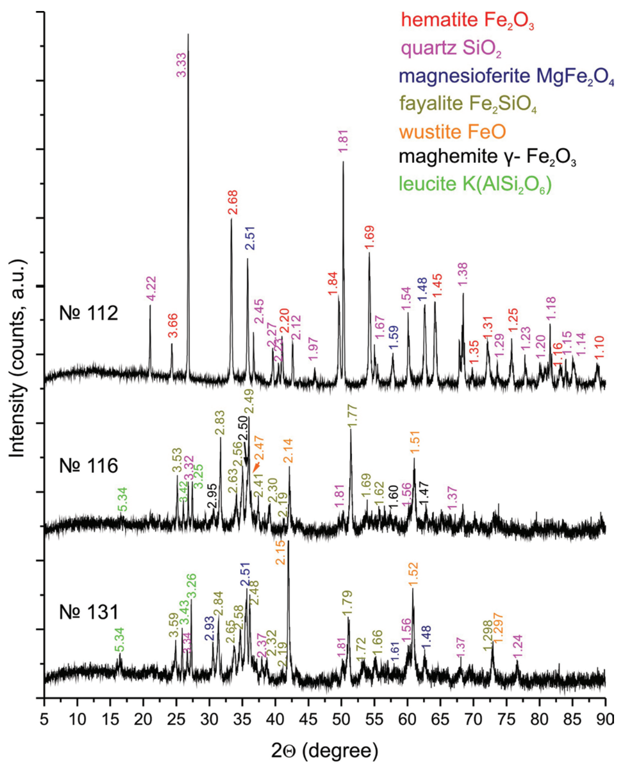

Fig. 1. PXRD patterns of studied samples

Table 1. Results from the XRF analysis (in wt%)

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3
No 112	<LOD	0.73	6.03	34.50	0.37	<LOD	0.95	0.70	0.27	0.09	56.31
No 116	0.52	0.48	9.54	32.55	0.68	0.09	4.40	6.28	0.34	0.11	44.90
No 131	0.42	0.40	7.12	28.75	0.60	0.13	5.02	5.61	0.24	0.10	51.46

LOD – limits of detection

sumed that the studied slags were formed at such low temperatures, based on detected quartz. Quartz is stable up to about 890 °C, then transforms into tridymite. Nevertheless, in PXRD patterns, the peaks of quartz are found up to about 1100 °C. Small amounts of tridymite may be present in the studied samples, but it was not registered due to the PXRD method limits of detection (Bitay et al., 2020).

According to the results obtained, can be assumed that iron reduction took place at lower temperatures of about 900 up to 1000 °C. The detected maghemite (sample 116) is a marker of poor ventilation control in the furnace, namely additional air supply to the furnace (Manasse et al., 2002).

A decrease in Fe_3O_4 wt% in the slag, compared to the studied ore by 11.41 wt% (sample 116) and 4.85% (sample № 131) was registered (Table 1). In ancient times, the iron extraction from the ore was about 10–12 wt% (which corresponds to 14.3–17.16 wt% Fe_3O_4), and the remaining amount of Fe from the ore was included in slag (Portillo et al., 2018). The smaller amount of extracted iron for sample 131 compared to sample 116 can be explained by the variable amount of quartz in the polymineral ore and/or additional air supply to the furnace.

Conclusion

The self-fluxing hematite ore was used for the realization of the ancient iron metallurgical process at the "Sladak Kladenets" and "Malko Dryanovo" archaeological sites. The quartz from the ore decreases the temperature of the iron reduction process to 900–1000 °C. The poor and casual ventilation control in the furnace leads to a wide variation of iron extraction (of about 50%).

The results obtained (phase composition of slags, operating furnace temperature, and ventilation control) are of archaeological importance and will contribute to the future chronological specification of the time of realization of the metallurgical process as well as of the type of used furnaces.

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References

Bitay, E., I. Kacsó, C. Tănăselia, D. Toloman, G. Borodi, S.-P. Pánczél, Z. Kisfaludi-Bak, E. Veress. 2020. Spectroscopic characterization of iron slags from the archaeological sites of Brâncovenești, Călugăreni and Vătava located on the Mureș County (Romania) Sector of the Roman Limes. – *Appl. Sci. 10*, 15, 5373; https://doi.org/10.3390/app10155373.

Friede, H., A. Hejja, A. Koursaris. 1982. Archaeo-metallurgical studies of iron smelting slags from prehistoric sites in Southern Africa. – *J. South African Inst. Min. Metallurgy*, *82*, 38–48.

Kanurkov, G. 1988. *Iron Ore Deposits in Bulgaria*. Sofia, Tehnika, 173–175 (in Bulgarian).

Kramar, S., J. Lux, H. Pristacz, B. Mirtič, N. Rogan-Šmuc. 2015. Mineralogical and geochemical characterization of Roman slag from the archaeological site near Mosnje (Slovenia). – *Materials and Technology*, *49*, 3, 343–348; https://doi.org/10.17222/MIT.2013.299.

Larreina-Garcia, D., Y. Li, Y. Liu, M. Martinón-Torres. 2018. Bloomery iron smelting in the Daye County (Hubei): Technological traditions in Qing China. – *Archaeol. Res. Asia*., *16*, 148–165; https://doi.org/10.1016/j.ara.2018.10.001.

Manasse, A., M. Mellini. 2002. Chemical and textural characterisation of medieval slags from the Massa Marittima smelting sites (Tuscany, Italy). – *J. Cultur. Herit., 3*, 3, 187–198; https://doi.org/10.1016/S1296-2074(02)01176-7.

Palmer, D. C., M. T. Dove, R. M. Ibberson, B. M. Powell. 1997. Structural behavior, crystal chemistry and phase transitions in substituted leucites: High-resolution neutron powder diffraction studies. – *Am. Miner*., *82*, 16–29; https://doi.org/10.2138/am-1997-1-203.

Portillo, H., M. C. Zuluaga, L. A. Ortega, A. Alonso-Olazabal, X. Murelaga, A. Martinez-Salcedo. 2018. XRD, SEM/EDX and micro-Raman spectroscopy for mineralogical and chemical characterization of iron slags from the Roman archaeological site of Forua (Biscay, North Spain). – *Microchem. J*., *138*, 246–254; https://doi.org/10.1016/j.microc.2018.01.020.

Portillo-Blanco, H., M. C. Zuluaga, L. A. Ortega, A. Alonso-Olazabal, J. J. Cepeda-Ocampo, A. Martínez Salcedo. 2020. Mineralogical characterization of slags from the Oiola site (Biscay, Spain) to assess the development in bloomery iron smelting technology from the Roman period to the Middle Ages. – *Minerals*, *10*, 4, 321; https://doi.org/10.3390/min10040321.

PDF (Powder Diffraction File). 2001. ICDD, Newtown Square, PA.

Roberts, B. W., C. P. Thornton. 2014. *Archaeometallurgy in Global Perspective: Methods and Syntheses*. New York, Springer New York, Imprint: Springer; http://dx.doi.org/10.1007/978-1-4614-9017-3.

Tsankov, Ts., L. Philipov, N. Katskov. 1995. *Explanatory Note to a Geological Map of Bulgaria on Scale M 1:100 000, Kazanlak Map Sheet*. Sofia, Geology and Mineral Resources Committee, Enterprise of Geophysical Survey and Geological Mapping, 61 p. (in Bulgarian).

Uzunov, Zh., I. Dimitrova, B. Dumanov. 2017. Results from the field archeological excavations of archeological sites in the working area. – In: *SARCHUS-AIR. Localization and Experimental Reconstruction of Ancient Roads and Habitats*. Sofia, Askoni publ., 37–49 (in Bulgarian).